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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

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So far as we can find, three triiodbenzols have been described in the chemical literature, but the constitution of only one has been established thoroughly; this is the unsymmetrical (1 . 2 . 4) isomere melting at 76° obtained by Kekulé * from the action of iodine and iodic acid on benzol. More recently Hantzsch † has also made it from the diiioddiazobenzol iodide prepared from diiodaniline and found that it melts at 77°.

The other two isomeric triiodbenzols were made by Istrati and Georgescu ‡ by heating together benzol iodine and concentrated sulphuric acid. Unfortunately their original paper is not at our disposal, so that we know their work only from the abstracts of it in the "Jahresbericht über die Fortschritte der Chemie" and Beilstein's Handbuch (third edition). From these it appears that they ascribed the unsymmetrical constitution (1 . 2 . 4) to their compound melting at 85°, and the adjacent structure (1 . 2 . 3) to that melting at 182° to 184°, but there is no statement that they determined these constitutions experimentally. The experiments of Kekulé and Hantzsch just cited prove that the unsymmetrical isomere melts at 77° (or 76°), and, therefore, their compound melting at 85° cannot have this structure.

Under these circumstances it seemed worth while to prepare the symmetrical triiodbenzol and to prove its constitution by experiment; accordingly we made the triiodaniline by the method of Michael and Norton, § that is, treating chloride of aniline with monochloride of iodine; and replaced the amido group in this body by hydrogen by means of the diazo reaction.

* Ann. Chem. (Liebig), CXXXVII. 164 (1866).

† Ber. d. chem. Ges., XXVIII. 684 (1895).

‡ Buletinul d. Soc. d. Sciinte Fiz. d. Bucuresci, I. 62. Jarhresb. Chem. 1892, 1063. Beilstein's Handbuch (3d Edition), III. 73.

§ Ber. d. chem. Ges., XI. 111 (1878).

The triiodbenzol thus obtained melted at 181°, which suggested that it was identical with the substance made by Istrati and Georgescu melting at 182° to 184°, and this was proved to be the case by treating it with fuming nitric acid, which converted it into a triioddinitrobenzol melting at 210°, whereas Istrati and Georgescu * under similar conditions obtained from their substance a dinitro derivative melting at 210°–212°. That our triiodbenzol had the symmetrical constitution (1 . 3 . 5) was very probable, because the trichloraniline and the tribromaniline made under similar conditions are symmetrical compounds; but, as we felt it was necessary to give an absolute proof of its structure, we treated the triioddinitrobenzol with aniline, when it formed a trianilidodinitrobenzol melting at 181°. The symmetrical trianilidodinitrobenzol made by Palmer and one of us † from symmetrical tribromdinitrobenzol melted at 179°; in spite of the difference of two degrees in these melting points there can be no doubt of the identity of the compounds, and it follows, therefore, that the triiodbenzol melting at 181° has the constitution I_3 1 . 3 . 5. This would leave only the structure 1 . 2 . 3 for Istrati and Georgescu's triiodbenzol melting at 85°; but in view of the fact that this compound was isolated from a mixture of the two triiodbenzols and two tetraiodbenzols, it seems to us possible that it may be the unsymmetrical isomere (1 . 2 . 4) (melting at 77°) contaminated with some of these less fusible substances. We had hoped to prepare several derivatives of the triiodbenzol, but were unable to do so in the time at our disposal, and, as we cannot continue our work together, think it well to publish this account of the results so far obtained.

Preparation of Triiodaniline.

The triiodaniline was prepared by the method of Michael and Norton ‡ slightly modified. Ten grams of aniline were dissolved in dilute hydrochloric acid, and diluted with water at 15° or a higher temperature to the volume of seven litres. This solution was then treated with a rapid stream of air charged with the vapor of monochloride of iodine by passing it through a flask containing somewhat more than the required amount of this substance heated to about 60° by immersion in warm water. After thirty or forty minutes the action had come to an end, and the liquid was filtered as quickly as possible to remove a heavy black precipi-

* Bul. Soc. Sci. Fiz., I. 66.

† These Proceedings, XXIV. 111.

‡ Ber. d. chem. Ges., XI. 111 (1878).

tate which had formed; the filtrate was allowed to stand for several hours, when it deposited a flocculent buff-colored precipitate, the weight of which varied from 10 to 20 grams in different operations; that is, 20 to 40 per cent of the theoretical yield. An additional amount of the triiodaniline could undoubtedly have been obtained from the black precipitate, which was filtered out at first, but this was so impure that it seemed more time would be lost in purifying it than in preparing fresh quantities of the second buff-colored precipitate, which without further treatment was pure enough for the manufacture of the triiodbenzol. That it was the triiodaniline was shown by an analysis of the substance purified by crystallization from glacial acetic acid and alcohol with the aid of boneblack, which gave 81.25 per cent of iodine instead of the 80.87 per cent required by the formula. Its melting point was 185°. Michael and Norton give 185½°.

The monochloride of iodine used in this work was made by the action of chlorine on iodine according to one of the methods given by Hannay,* and used later by Bornemann.† Bunsen's ‡ method, which consists in boiling iodine with aqua regia, gave a less good result. Distillation of iodine with potassic chlorate, recommended by Schutzenberger § and Hannay,‖ was not tried. Forty-two grams of powdered iodine (the amount needed for ten grams of aniline) were treated with dry chlorine in a flask, until they had gained 12 grams; in addition to the reddish brown liquid monochloride a considerable amount of the brilliant yellow crystalline trichloride of iodine was formed, which was converted into the monochloride by adding a small excess of iodine and heating the flask gently on the steam bath under a short air condenser, until the yellow crystals had disappeared. The monochloride of iodine solidified in fine gray crystals, if cooled below 10°, and in this solid state could be kept for some time without decomposition. Its tendency to solidify made it necessary in the preparation of triiodaniline to use the solution of chloride of aniline at a temperature of at least 15° in order to avoid the danger of having the tube stopped up with monochloride of iodine. Although this substance melts at 24°.7 (Hannay), we found no trouble from solidification with a solution at 15°, which can be explained by the marked tendency of the monochloride to remain liquid after it has been melted.

* Proc. Lond. Chem. Soc., XXVI. 815 (1873).
† Ann. Chem. (Liebig), CLXXXIX. 184 (1877).
‡ Gmelin-Kraut's Handbuch, I. 2, p. 416.
§ Zeitschr. d. Chem., VI. 1.
‖ Proc. Lond. Chem. Soc., XXVI. 815 (1873).

Symmetrical Triiodbenzol, $C_6H_3I_3$.

This substance was prepared as follows: Ten grams of the buff-colored triiodaniline, made as described in the previous section, were boiled with 125 c.c. of benzol and 25 c.c. of alcohol, and disregarding the undissolved portion, 5 c.c. of commercial sulphuric acid were added, and then 5 grams of finely powdered sodic nitrite were sifted into the liquid as quickly as possible. As soon as the evolution of nitrogen had slackened sufficiently, the liquid was boiled for some time on the steam bath, until a large part of the solvents had passed off; during this boiling a bright yellow solid, which formed on the particles of sodic nitrite as they entered the liquid, changed its color to a light grayish brown. After the solution had been boiled, it was allowed to stand over night, and then the deposit was filtered out and washed, first with alcohol and afterwards with hot water, to remove the inorganic salts. The amount of this crude product rarely fell below 50 per cent of the theoretical yield.

The product, obtained as described above, was next sublimed from a large watch-glass heated on the sand bath, and covered with a funnel which stood on a piece of filter paper above the substance. If this sublimation was carried on slowly enough, as much as 80 per cent of white glistening crystals was obtained, but if it was urged too fast, the impurities also sublimed, and the crystals were yellow, or even in extreme cases light brown and sticky. When proper care was used, white crystals were obtained by this sublimation, even from very impure products, such as those recovered by evaporating the liquid portion of the product of the diazo reaction. The white sublimed crystals were not, however, pure, and to remove from them a persistent impurity we found repeated recrystallizations from alcohol were necessary, which finally raised the melting point to 181°, where it remained constant. The substance was then dried at 100°, and analyzed with the following results: —

I. 0.1187 gram of the substance gave by the method of Carius 0.1838 gram of argentic iodide.

II. 0.1453 gram gave 0.2249 gram of argentic iodide.

	Calculated for $C_6H_3I_3$.	Found. I.	Found. II.
Iodine	83.54	83.66	83.60

Properties of 1.3.5 *Triiodbenzol.* — This substance crystallizes from alcohol at first in radiating groups composed of a few slender prisms, which develop later into long white prisms frequently tapering, but

always terminated by a single plane at an oblique angle to the sides of the prism. It melts at 181°, and sublimes easily. It is freely soluble in benzol, or carbonic disulphide even in the cold; in chloroform it is moderately soluble in the cold, freely soluble when hot; in ether it is moderately soluble, whether hot or cold; in glacial acetic acid or ethyl acetate it is somewhat soluble in the cold, freely soluble when hot; in alcohol or acetone it is slightly soluble in the cold, moderately soluble when hot; it is apparently insoluble in water, hot or cold. The best solvent for it is alcohol. Strong hydrochloric acid has no apparent action on it, even when hot; strong nitric acid also has little or no action on it, but fuming nitric acid acts on it in the way described in the next paragraph. Strong sulphuric acid, when heated with it to its melting point, causes a partial decomposition, taking on a dark color; at higher temperatures the triiodbenzol sublimes out of the mixture. A strong solution of sodic hydrate seems to have no action on it, even when boiling.

An attempt was made to prepare triiodnitrobenzol; for this purpose five grams of symmetrical triiodbenzol were boiled with 140 c.c. of a mixture consisting of four parts of fuming nitric acid with one part of common nitric acid. On cooling light yellow crystals appeared, and an additional amount of the product was obtained by pouring the acid liquid into about a litre of water, when a pale yellow flocculent precipitate was formed, which was filtered out, after it had stood some time, and with the crystals weighed 5.3 grams. This was purified by crystallization from a mixture of four parts of alcohol with one of water, until it showed the constant melting point 210°. This indicates that the substance is triioddinitrobenzol, since Istrati and Georgescu * obtained a triioddinitrobenzol melting at 210°–212° from their triiodbenzol melting at 182°–184°. For still greater certainty the substance was dried at 100°, and analyzed with the following result: —

0.2049 gram of the substance gave by the method of Carius 0.2644 gram of argentic iodide.

	Calculated for $C_6HI_3(NO_2)_2$.	Found.
Iodine	69.77	69.76

The substance, therefore, is a dinitro compound, although obtained from fuming nitric acid somewhat diluted with common nitric acid. We

* Bul. Soc. Sci. Fiz., I. 66.

did not have time to try whether the mononitro compound could be obtained with a still more dilute nitric acid.

The agreement between the melting points of our triiodbenzol, 181°, and triioddinitrobenzol, 210°, with those obtained by Istrati and Georgescu, * 182°–184° and 210°–212°, establishes the identity of these substances beyond a doubt. The triioddinitrobenzol also gives us the means of proving their constitution. For this purpose 0.5 gram of the triioddinitrobenzol were heated with 0.5 gram of aniline; this proportion gives about six molecules of aniline to each molecule of the dinitro compound. The heating was carried on for two hours on the steam bath, and the product, a dark red solution, was freed from the excess of aniline by washing with dilute hydrochloric acid, when it formed a dark red sticky mass, which was purified by working it well with a rod under dilute hydrochloric acid and then crystallizing it from alcohol. It showed the constant melting point 181°, which agrees sufficiently well with 179°, that given by Palmer and one of us † for the trianilidodinitrobenzol made from the tribromdinitrobenzol Br_3 1 . 3 . 5 . $(NO_2)_2$ 2 . 4. This proves, therefore, that the triiodbenzol melting at 181° has the iodine in the position 1 . 3 . 5, as would have been inferred from its preparation from triiodaniline, which according to the analogy of the chlorine and bromine compounds should have the symmetrical constitution.

* Bul. Soc. Sci. Fiz., I. 62, 66.

† These Proceedings, XXIV. 111.